arXiv:cond-mat/0209344v1 [cond-mat.mtrl-sci] 15 Sep 2002

# Coupling time scales for simulation of structure transformation: an attempt to combine molecular dynamics and phase-field theory

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## Abstract

A multiscale scheme combining molecular dynamics (MD) and microscopic phase-field theory is proposed to study the structural phase transformations in solids with inhomogeneous strain field. The approach calculates strain response based on MD and atomic diffusion based on the phase field theory. Simulations with the new technique are conducted in two examples. The first involves interface roughening in a Co/Cu thin film, where interfacial undulations due to lattice mismatch is demonstrated. The second example is a study of spinodal decomposition in AgCo/Pt/MgO(001) thin film, where we show that Co atoms are attracted by dislocations in the Pt/MgO interface, producing an interesting nanostructure.

PACS: 64.75.+g, 68.35.Ct, 02.70.Ns, 68.55.-a

Typeset using REVTEX

Phase-field theory[1] and molecular dynamics[2] (MD) are both important theoretical tools to investigate the phase transformation in solids. In particular, phase-field theory has been frequently used to simulate the structure evolution of micro/mesoscopic morphology during phase transformations. A key factor to this capability lies in the flexibility of time scale used in the theory: one can always choose to trace the evolution of field variables whose dynamic evolution is "slow" compared to the remaining microscopic degrees of freedom. To incorporate the effect of elastic strains that are responsible for the formation of various mesoscale morphological patterns, continuum elasticity theory is usually used to calculate the strain energy induced by the lattice mismatch.[1,3] However, a priori assumption on the transformation outcome has to be made because the elastic constants of the outcome phases are needed in the calculation. This may seriously reduce the predictive ability of the phase-field theory (especially the microscopic phase field model). In addition, the general formula of strain energy in various situations is often difficult to obtain. The second shortcoming of the phase-field theory comes from its assumption of coherent microstructure. It is not suitable for describing dislocations and their corresponding strain effect at an incoherent interface between two different phases. On the other hand, the method of molecular dynamics directly simulates the motion of moleculars by solving Newton's equations. MD is highly effective in relaxing the local atomic distances and thus evaluating the stain energy. MD calculations are able to predict equilibrium and nonequilibrium properties of condensed systems. Despite of these advantages, MD has not been used to model dynamical morphological evolution in phase transformations. The main problem is that the characteristic time scale of MD is too short (∼1 ns with time step ∼1 fs) compared with that of most phase transformation phenomena.

In this paper, an approach is developed to combine the microscopic phase-field theory and molecular dynamics to overcome the above difficulties. Two simple systems are investigated to illustrate how the new method works.

In MD, the variables to simulate are the atomic positions, $\{\mathbf{r}_i\}$, which evolve according to Newton's equation:[2]

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = -\nabla_i V(\{\mathbf{r}_i\}), \tag{1}$$

where $V(\{\mathbf{r}_i\})$ is the empirical potential. For the microscopic phase-field theory, the variables considered are the site occupation probabilities, $\{n_i\}$. The value of $n_i$ represents the probability to find a solute atom at the $i$-th lattice site. The evolution equation is given as[1]

$$\frac{dn_i}{dt} = \sum_j L_{ij}\mu_j = \sum_j L_{ij}\frac{\partial F(\{n_i\})}{\partial n_j}, \tag{2}$$

where $\mu_j$ is the chemical potential at the $j$-th site and $L_{ij}$ is the kinetic coefficient proportional to the inverse average time of elementary diffusional jumps from site $i$ to $j$, and $F$ is the free energy function.

In our method, both the lattice position and the occupation probability, $\{\mathbf{r}_i, n_i\}$, are considered as variables. Here, $\mathbf{r}_i$ are used to describe local atomic motion such as strain response or dislocation, and $n_i$ are used to describe atomic diffusion between different lattice sites. With mean-field approximation, the empirical potential and free energy can be expressed as functions of both atomic position and composition, i.e., $V(\{\mathbf{r}_i, n_i\})$ and $F(\{\mathbf{r}_i, n_i\})$. For example, when the pair potential is considered, $V(\{\mathbf{r}_i, n_i\})$ in the current approach can be written as:

$$V(\{\mathbf{r}_i, n_i\}) = \frac{1}{2}\sum_{i,j}\left[n_i n_j V_{AA}(\mathbf{r}_i - \mathbf{r}_j) + 2n_i(1-n_j)V_{AB}(\mathbf{r}_i - \mathbf{r}_j) + (1-n_i)(1-n_j)V_{BB}(\mathbf{r}_i - \mathbf{r}_j)\right]. \tag{3}$$

The evolution of atomic position $\{\mathbf{r}_i\}$ is conducted according to Eq. (1) with the new potential $V(\{\mathbf{r}_i, n_i\})$. When the elastic equilibrium is reached, $\{\mathbf{r}_i\}$ satisfy the following equations:

$$\frac{\partial V(\{n_i, \mathbf{r}_i\})}{\partial \mathbf{r}_i} = 0. \tag{4}$$

Since the free energy depends on $\{\mathbf{r}_i\}$ only via $V(\{\mathbf{r}_i, n_i\})$, one has

$$\frac{\partial F(\{n_i, \mathbf{r}_i\})}{\partial \mathbf{r}_i} = 0. \tag{5}$$

Since diffusion is much slower than elastic response, we can assume that the system is in elastic equilibrium during the diffusion process. The diffusion equations are:

$$\begin{aligned}\frac{dn_i}{dt} = \sum_j L_{ij}\mu_j &= \sum_j L_{ij}\frac{dF(\{\mathbf{r}_i, n_i\})}{dn_j} \\ &= \sum_j L_{ij}\left[\frac{\partial F(\{\mathbf{r}_i, n_i\})}{\partial n_j} + \sum_k \frac{\partial F(\{\mathbf{r}_i, n_i\})}{\partial \mathbf{r}_k}\cdot\frac{d\mathbf{r}_k}{dn_j}\right] \\ &= \sum_j L_{ij}\frac{\partial F(\{\mathbf{r}_i, n_i\})}{\partial n_j}, \end{aligned} \tag{6}$$

where $dF(\{\mathbf{r}_i, n_i\})/dn_j$ means that $\{\mathbf{r}_i\}$ is function of $n_j$ and the differential with respect to $n_j$ should also operat on $\mathbf{r}_i$. The elastic equilibrium conditions Eq. (5) is used to obtain the final result of Eq. (6). In the numerical scheme, $m$ MD steps with time interval $\delta t$ are conducted to reach the elastic equilibrium state before every diffusion step with time interval $dt$. It is a multiscale scheme since $m\delta t \ll dt$.

In order to illustrate how the method works in practice, we first consider interface roughening in a heteroepitaxial thin film system.

In uniform heteroepitaxial thin films, there usually exists large stress arising from the lattice mismatch between thin film and substrate. To reduce the strain energy, surface roughening by mass diffusion occurs during film growth or annealing.[4] The length scale of surface roughening is about a few hundred nanometers,[4] which is too large for the current atomic simulation. We alternatively simulate a similar process, the interface roughening, to demonstrate the effect of strain on the mass transport.

The system studied here is Cu-Co system where the lattice mismatch is about 2%. Cu and Co is immiscible in the bulk with a mixing energy of +13 kJ/g atom.[5] Atomic interaction among Cu and Co atoms is described with the Tight-binding second-moment-approximation (TB-SMA) potential.[6] The potential parameters for the pure species are available in the literature,[6] while the cross parameters (Cu-Co) are evaluated by fitting the mixing energy and the lattice length of the disordered phase within the mean-field approximation. We consider a coherent Co film grown on Cu substrate. The as-grown film (initial state) has flat surface and interface [Fig. 1(a)]. The evolution of phase morphology is simulated by the above method, with result shown in Fig. 1(b). It reveals interfacial undulations with varying amplitude and wavelength. The undulation of interfacial increases the interfacial energy while decreases the strain energy. The total energy decreases in such process. In comparison with surface roughening,[4,7] no groove or cusp is found in the current simulation of interface roughening.

As the next example, we consider the spinodal decomposition of a thin film on a periodically strained substrate.

Adsorbed layers epitaxially grown on single-crystal surfaces are generally strained due to the lattice mismatch. In the weakly incommensurate situation such as Ag layers grown on Pt(111) surface,[8] highly ordered periodic dislocation network is formed to relieve the mismatch strain, hence invalidating the assumption of coherent microstructure usually adopted in the phase field theory. Such dislocation pattern can be used to fabricate interesting metal island arrays in two-dimension.[9] If the second alloy film is grown on this strained film and the second film is unstable to spionodal decomposition, it may be expected that the dislocation network will act as a preferred length scale for the spinodal decomposition. To investigate this issue, we simulate the spinodal decomposition in a AgCo/Pt/MgO(001) thin film system.

For Pt films deposited onto a (001) MgO substrate, a dislocation network with periodicity 4.05 nm is predicted.[10] We consider the growth of AgCo on the strained Pt/MgO thin film and simulate the spinodal decomposition of the AgCo phase. The potential between Ag-Co-Pt is adopted as TB-SMA potential.[6] For simplicity, the interaction between Pt and MgO is approximated as the Lenard-Jones potential by fitting the adsorption energy and atomic distance.[11] MgO atoms are kept fixed (with crystal lattice of 4.21 Å) in simulation. For the initial state, Pt atoms are arranged in their ideal lattice sites (with a lattice parameter of 3.924 Å), and a dislocation network between Pt and MgO naturally forms in the simulation. The initial AgCo phase is assumed to be coherent with Pt and is disordered with an average composition $n_i = 0.5$. A simulation result of the thin film with 3 monolayer (ML) of Pt and 10 ML of AgCo is shown in Fig. 2. The atomic configuration with dislocation network and the corresponding strain effect are demonstrated in Fig. 2(a) and 2(b) for the initial stage before atomic diffusion occurs. It can be seen that large strain is concentrated near the dislocation cores. The final result of phase transformation is depicted as Fig. 2(c). It shows that Co atoms segregate in strained regions because they are smaller in size. Within a few layers near the AgCo/Pt interface, Ag atoms gather in less strained regions and produce an interesting nanostructure. The surface layers are occupied by Ag atoms since the surface energy of Ag (1.30 $J/m^2$) is smaller than that of Co atoms (2.71 $J/m^2$).[12] It is interesting that some Pt atoms above the dislocation are "pulled up" by Co atoms in Fig. 2(c), which reflects the important interaction between Pt substrate and AgCo film. Such effect can not be described within the coherency approximation.

The method presented here is on the microscopic level. Similar to other atomic scale simulations, one of its disadvantage is that the system size simulated is relatively small compared to mesoscale morphology. In contrast, continuum field theories have more freedom in changing the length scale of simulation. Such theories can be expected to couple with computational mechanics methods such as the Finite Element method by a similar coupling approach as described here. This is not pursued in this paper.

This work was supported by a Max Planck Post-Doc Fellowship for ZL and by US National Science Foundation through Grant CMS-0085569. We thank Prof. Long-Qing Chen at the Pennsylvania State University for helpful discussions. The code of MD simulation in this work comes from the program GONZO of Stanford Multiscale Simulation Laboratory (MSL).

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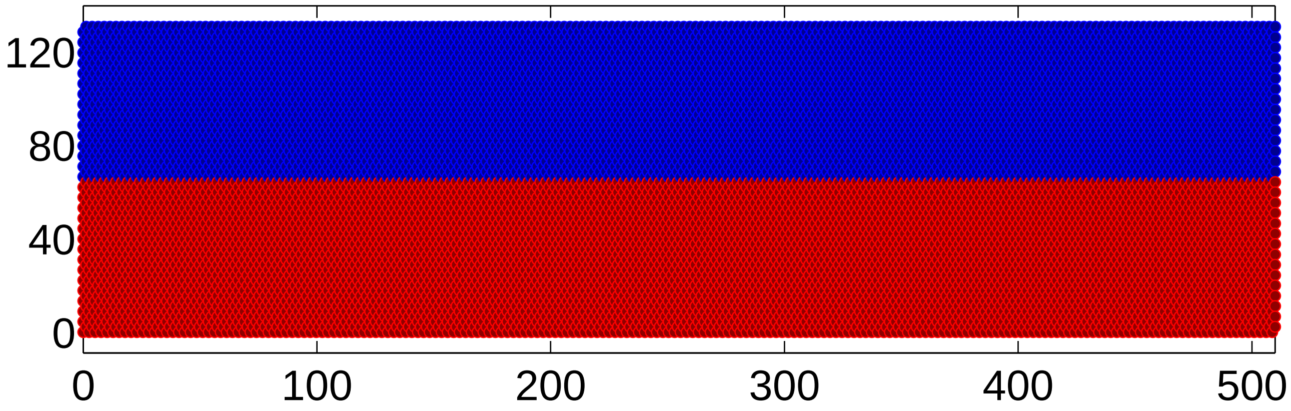
# FIGURES

FIG. 1. Interface roughening for a Co film grown on Cu substrate. The Cu phase is colored in red while the Co phase blue. The axes have length unit of Å. The system is composed of $200 \times 60 \times 1$ atoms. Periodic boundary conditions are adopted in the $x$- and $z$-directions while free boundary conditions in the $y$- direction. (a) The as-grown film (initial state of simulation). (b) The simulation result of interface roughening.

FIG. 2. Dislocation, strain effect and spinodal decomposition in a AgCo/Pt/MgO(001) thin film. (a) Atomic configuration of the as-grown film before the spinodal decomposition of Ag-Co occurs. The blue hollow circle ($\circ$) and cross ($+$) represent O and Mg atoms, respectively. The green stars ($*$) are Pt atoms, and the red filled circles ($\bullet$) are disordered AgCo atoms with occupation probability $n_i = 0.5$. (b) The atomic displacement of the as-grown film in (a). Strain field is caused by dislocations between Pt and MgO. (c) The resulting configuration after phase transformation. The occupation probability of Ag-Co phase is visualized by the color scheme shown in the colorbar.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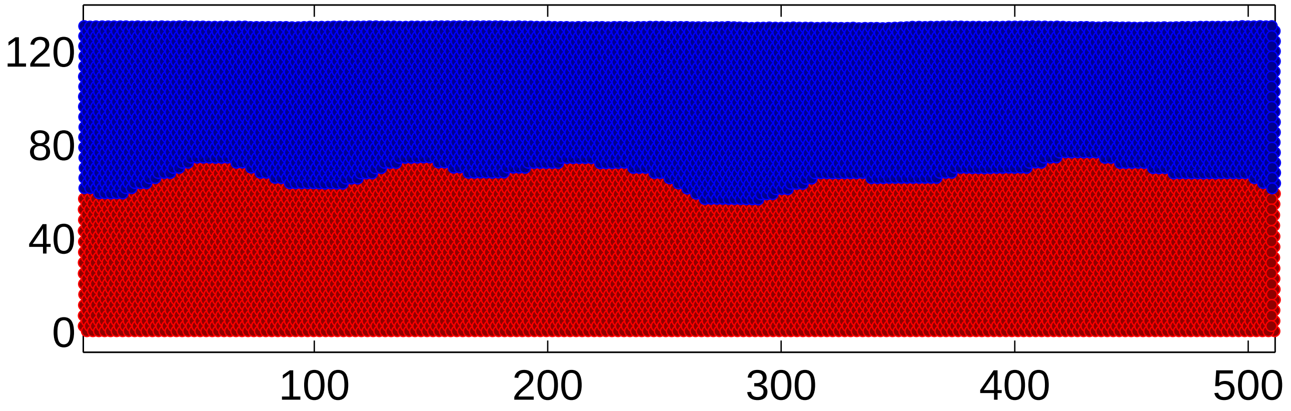
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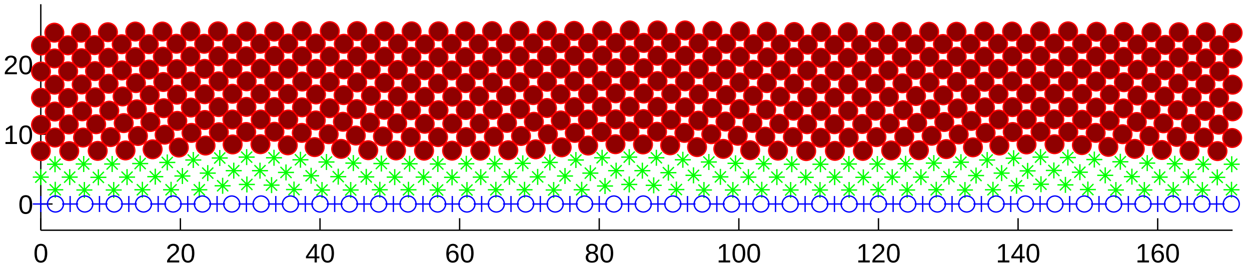
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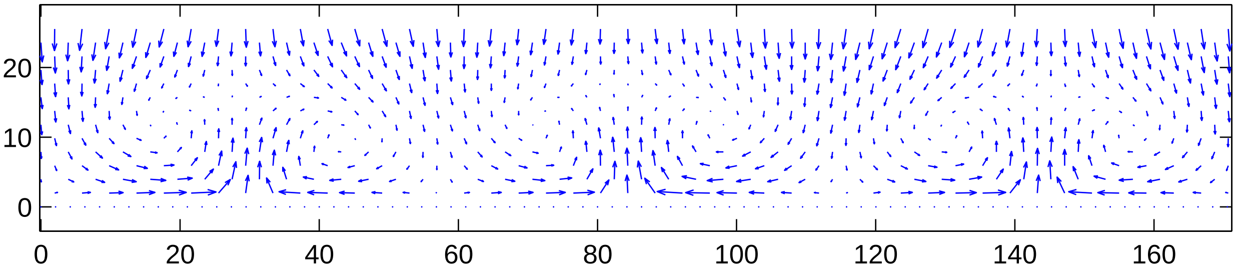
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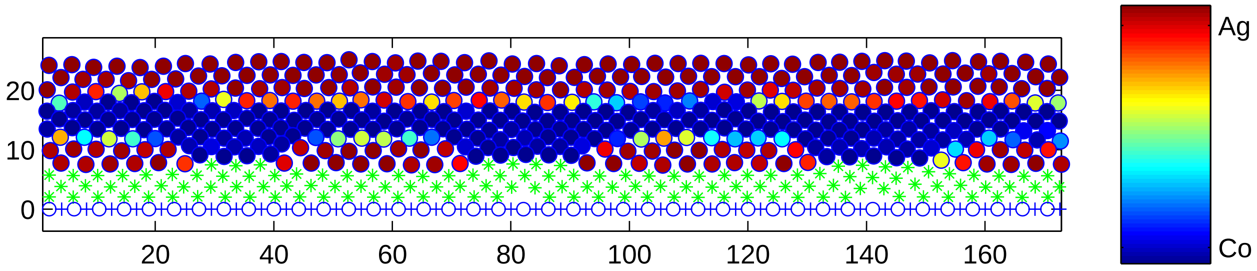
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